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Postsynthesis Transformation of Three-Dimensional Framework into a Lamellar Zeolite with Modifiable Architecture

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Supporting Information

ABSTRACT: Mild treatment of zeolite UTL results in degradation of its structure with preservation of the initially present dense layers connected by D4R "bridges". The lamellar product obtained through this 3D to 2D zeolite conversion has been structurally modified similar to methodologies applied to layered zeolite precursors, which show the opposite 2D to 3D zeolite transformation.

The large pore 14 × 12-ring UTL framework was discovered to undergo structural change in an aqueous environment that is consistent with conversion into a lamellar material by degradation of the D4R units originally supporting its dense layer regions. This is diagnosed using X-ray powder diffraction characterization (XRD). Subsequent changes upon various treatments developed previously for investigation of layered zeolites such as calcination, stabilization, and swelling, further support the lamellar structure of the product (denoted IPC-1P; calcined form IPC-1; IPC = Institute of Physical Chemistry) and its potential for structural modification. The behavior of IPC-1P matches that of well-established layered zeolite derivatives like the MCM-22 family; however, it provides a completely new mode of preparation, i.e. from a 3D framework. Additional characterizations, including nitrogen sorption, FTIR, TEM, and powder pattern simulations, are consistent with conclusions derived from XRD. This is the first example of the conversion of a 3D zeolitic framework into a new 2D material, which can be further modified structurally.

Zeolite UTL is notable for its attractive large pore system combining 14-ring pores intersecting with 12-rings with dimensions 0.95 × 0.71 nm^2 and 0.85 × 0.55 nm^2, respectively.[1] The UTL framework was first obtained as germanosilicate IM-12[2] and ITQ-15 with Si/Ge molar ratios lower than 10.[3] The critical parameters of the formation of UTL with a variety of structure directing agents have been extensively studied recently.[4,5] The structure of UTL can be viewed as dense 2D sections, layers, separated by D4R bridging units, pillars. The adoption of this description will become apparent later on. The layer has the same $x-y$ projection as that of zeolite ferrierite, but in the z-direction it has a more complicated connectivity and corresponding longer repeat, i.e. 1.25 nm vs 0.75 nm.[4] These relationships (Figure 1, further illustrated in Supporting Information, Figure SI 1) are relevant as defining the lower limit for the thickness of the 'UTL layer' as roughly 0.9−1 nm.

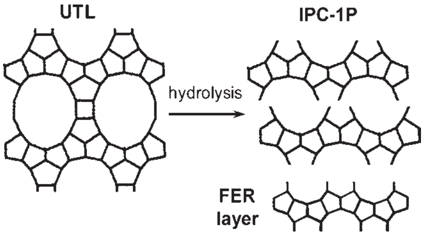

Figure 1. Transformation of UTL into layered zeolite; the included FER layer shows similarity with the UTL layer projection.

In this contribution we report on the discovery that the originally 3D structure of UTL zeolite in its porous form is unstable and can be postsynthetically transformed in an aqueous environment into a lamellar solid, apparently with preservation of the structural integrity of the layers. We established this initially using X-ray powder diffraction and further validated with TEM electron microscopy, theoretical simulations, chemical analysis, FTIR spectroscopy, and porosity measurements. Furthermore, we carried out various treatments conducive to modification of interlayer separation similar to those developed with layered zeolite precursors, like MCM-22P.[6] These treatments included calcination giving a contraction producing new microporous material IPC-1, intercalation of cationic surfactants with swelling and stabilization referred to as producing interlamellar expanded zeolite (IEZ; denoted here IPC-2). The results support the postulated lamellar architecture that can be modified by intercalation and related treatments. This finding represents the first example of the conversion of a 3D zeolite framework into a layered zeolite derivative (3D to 2D transformation). References 7 and 8 describe a reversible 2D to 3D transformation in a Ti-MWW system; however, this does not entail formation of a novel structure or layers and is without offering further a modifiable architecture. The described UTL system contrasts with the standard behavior of zeolite layered precursors,[9] which convert into 3D frameworks by condensation of layers (2D to 3D transformation), recognized to date as usually irreversible. Of course, in the case of UTL the reverse

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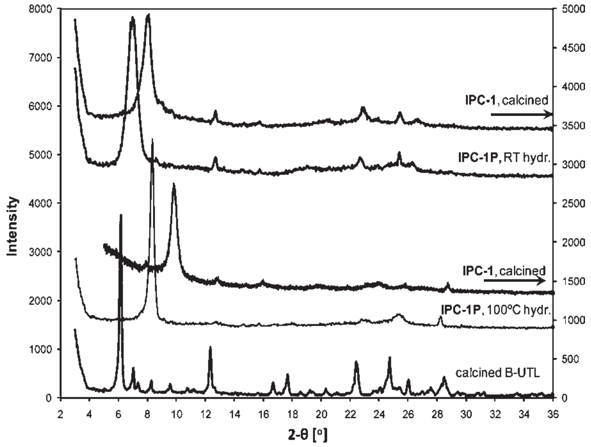

Figure 2. X-ray diffraction patterns of UTL zeolite and the products obtained after treatment in water. Samples treated under different conditions differ in the extent of contraction.

process, i.e. restoration of the original D4R bridge, is also highly improbable.

We studied several UTL calcined crystalline samples with different framework compositions having a Si/Ge molar ratio of about 2:1 with a 0 to 0.11 molar fraction of the oxide content of $BO_{1.5}$. The samples were subjected to hydrothermal treatment from room temperature up to 100 °C at a pH range from neutral to acidic (0.1 M HCl). All studied UTL materials showed profoundly altered X-ray powder diffraction (XRD) characteristics indicating significant structural change. We will refer to this reaction as hydrolysis. The initial UTL X-ray powder patterns with an abundance of diffraction lines (Figure 2) were reduced to several low intensity peaks (typically recorded in the range 3°—40° using Cu Kα radiation) and a dominant reflection with a somewhat variable 2-θ position corresponding to the *d*-spacing 1.2 ± 0.1 nm, dependent on initial sample and hydrolysis conditions. Several additional XRD patterns (Supporting Information, Figures SI 2—SI 5) and Figure 2 identify intralayer reflections of the UTL framework (with Miller indices (0*kl*)) obtained from the list of reflections provided on the IZA Web site.[1] The dominant peak is attributed to a new, shorter crystallographic repeat in the direction of layer stacking. The comparison of indexed patterns of the original UTL with the hydrolyzed one suggests that interlayer reflections having (*hkl*) with *h* not equal to zero appear to be absent while the position of the low intensity peaks should be reflections without the *x*-axis component (i.e., with (0*kl*) indices). In detail, there were some discrepancies in the exact peak positions and an uncertain assignment, but the conclusion that we were dealing with layers defined by the UTL framework was well justified. Subsequent treatments (see next paragraph) to change the interlayer spacing produced visible changes in the position of the aforementioned dominant peak while the pattern of the small mostly or entirely intralayer peaks was in general invariant, supporting the presumption of structural changes with retention of the UTL layer structure. Further support for this interpretation comes from the X-ray diffraction pattern simulated based on the 2D slab formed from the parent UTL zeolite (Supporting Information, Figure SI 6).

We also obtained TEM images of the sample with views perpendicular to the layer stacking, one of which (representative of many others) is shown (Figure 3). The obtained resolution is not atomic but clearly shows stacked layers with a roughly 1.1 nm repeat.

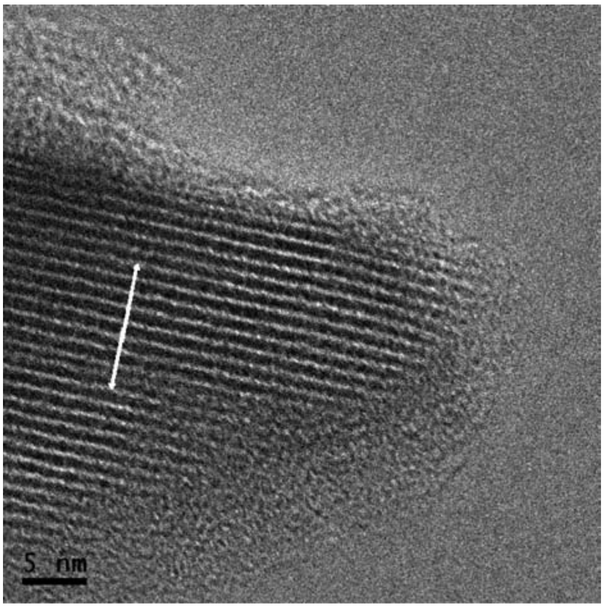

Figure 3. TEM imaged of the IPC-1P crystal in cross section; the white arrow represents 10 nm in length.

The hydrolysis causes contraction of the interlayer space that depends on the boron content, use of water or acid solution, and to a large extent the temperature of the hydrolysis. For example the material represented by two top XRD profiles (Figure 2) was treated at room temperature and showed a relatively large interlayer spacing: a low angle line in XRD at ca. 7° 2-θ Cu Kα (*d*-spacing 1.25 nm) and upon calcination at around 8° 2-θ (1.1 nm). It also appeared less degraded as the generally low intensity (0*kl*) diffraction lines were more distinct than those for the other sample in Figure 2. The latter was treated at near the boiling temperature of water, and it showed the low angle line at 8.3° 2-θ (1.07 nm). Upon calcinations its low angle line shifted to 9.8° 2-θ (0.9 nm). This latter shift of the dominant (interlayer) peak reveals a new small reflection at ca. 7.8° (1.13 nm), consistent with the (001) intralayer reflection in UTL. We conclude that it was previously obscured due to overlap with the former high intensity broad interlayer reflection. As the latter shifted due to vertical structure contraction the expected invariant (001) reflection having apparently inherent low intensity could be observed. It should be noted that the discussed small intralayer peaks with expected invariance upon treatments show slight deviations from the expected positions, i.e. those observed before treatment. This may be simply an instrument/data collection issue, which we tried to address, but it is also possible that the source is in the sample itself due to loss of heavy elements with a large radius (Ge) from the framework. This might entail unit cell contraction similar to the well-known dealumination of faujasite. We hope to resolve these ambiguities by detailed comprehensive studies in the future.

Table 1 shows the chemical analysis of the original UTL sample and those related (vide supra) to IPC-1, ICP-1SW, and IPC-2. Chemical analyses provided clear evidence that post-synthesis modifications led to a major removal of B and Ge from the samples. It can be inferred that particularly D4R units and their connectivities to the original layers were broken. This is in line

Table 1. Chemical Compositions of As-Synthesized B-UTL and Modified Samples; Representative Textural Data for Analogous (or Related) Samples Are Also Included

	Element mol %							
Sample	Si	Ge	B	Si/Ge	Si/B	BET (m^2/g)	V_{micro} (cm^3/g)	V_{meso} (cm^3/g)
B-UTL	85.4	13.6	1.0	6	85	458	0.193	–
IPC-1	95.5	4.3	0.2	22	480	270	0.095	–
IPC-1SW	97.3	2.6	<0.01	37	>10 000	216	0.007	0.123
IPC-2	97.2	2.8	<0.01	35	>10 000	313	0.139	–

with FTIR measurements. Skeletal vibrations of samples after the treatments were not substantially changed (Figure SI 7), evidencing the preservation of the original layers. In contrast, complete loss of B−OH groups and silanol nests after sample treatments evidenced by IR confirmed structural changes and chemical analysis data (Figure SI 8).

We measured the nitrogen isotherm of the calcined hydrolyzed UTL, which is apparently a novel material, and we chose to denote it IPC-1. It showed a typical microporous profile with a micropore volume of 0.095 cm^3/g and BET of 270 m^2/g with no mesoporous character. Textural properties illustrated by representative samples are shown in Table 1.

To further confirm and explore the evident lamellar nature of the uncalcined hydrolyzed UTL derivative IPC-1P, we subjected various samples to treatments similar to those for MCM-22 precursors and other zeolites,[6] such as stabilization in the expanded form and swelling. The former aimed to produce the so-called intralamellar expanded zeolite (IEZ) form according to treatments described in the literature.[10] The standard treatment, i.e. reaction with a silylating agent in the nitric acid solution and calcination, afforded a unique product, IPC-2, that did not show collapse to the standard calcined version (*d*-spacing ca. 0.9 nm) but in fact a revealed a *d*-spacing that was slightly greater than that in the starting material, i.e. 1.15 nm (Supporting Information). Nitrogen sorption determination gave a micropore volume of 0.139 cm^3/g and BET of 313 m^2/g, clearly higher than those of untreated IPC-1 (Table 1).

Another standard treatment performed for the lamellar IPC-1P was swelling similar to the one first carried out for MCM-22.[11] The sample was treated with a mixture of 25% cetyltrimethylammonium chloride (CTMA-Cl) and 40% tetrapropylammonium hydroxide (TPA-OH) with roughly 10:1 w/w (approximate pH around 13). The isolated solid product showed an X-ray pattern (Supporting Information, Figure SI 5) dominated by low angle peaks, clearly orders of each other with the *d*-spacing of the first one equal to 3.9 nm. The pattern is consistent with the $CTMA^+$ expanded (swollen) layered UTL derivative, but such patterns while a 'necessary proof' need to be interpreted with some caution as usually not 'sufficient proof' on their own as they may arise due to other materials (e.g., MCM-41 or M41S that can form under the applied conditions upon dissolution of a part of the zeolite).[6] The measured *d*-spacing repeat, 3.9 nm, is consistent with a swollen material with a UTL layer, which has an ∼1 nm thickness while the 'swelling' surfactant bilayer should be 2.5−3.0 nm thick as observed in the case of swollen MCM-22[9] and measured for the CTMA bilayer[12] on silica.

The swollen sample was calcined and the resulting XRD pattern (Supporting Information) was very similar to that of calcined hydrolyzed UTL, indicating retention of the layer structure upon treatment, which is relatively severe and could be destructive with the possibility of generating M41S type materials. The nitrogen isotherm for this material showed a BET area equal to 216 m^2/g, being lower than that for the IPC-1 (IPC-1P used for swelling, after calcination). This confirms small if any formation of mesoporous contamination such as M41S or MCM-41, upon swelling. The standard approach to further validation of swelling is subsequent pillaring as well as delamination as demonstrated and discussed with MCM-22P.[13] This work is underway.

The presented results show for the first time that germanosilicate UTL zeolite with or without boron can be converted into a lamellar material with zeolite-like layers (3D to 2D conversion). This new lamellar material denoted IPC-1P can be further modified in a way similar to the case of other layered solids. A novel procedure for conversion of 3D zeolite to 2D slabs presented here may be extended to other frameworks with similar structural features enabled by degradation of interlayer connectors (e.g., NU-87). It is clear that layered materials with similar physical and chemical properties as zeolites are interesting both for fundamental research and for potential applications in catalysis and other fields.

■ ASSOCIATED CONTENT

Supporting Information. Experimental procedures, synthesis of B-UTL, postsynthesis treatments, characterization of prepared materials, comparison of the *x*−*y* projection of UTL with FER and the view of the UTL and FER layer, and XRD patterns and comparison of the experimental and simulated pattern for the B-UTL sample hydrolyzed at room temperature are included in the Supporting Information. This material is available free of charge via the Internet at http://pubs.acs.org.

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